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Vibrational spectral studies and thermodynamic functions of 4,6-dihydroxy-5-nitro pyrimidine

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Abstract The vibrational spectra of 4,6-dihydroxy-5-nitro pyrimidine have been reported alongwith their assignments. Hydrogen bonding and tautomeric forms have been discussed. Thermodynamic functions have also been computed using the vibrational frequencies of the said molecule and the results discussed.

Keywords Infrared and Raman spectroscopy, vibrational frequencies, thermodynamic functions

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1. Introduction

Pyrimidine, cytosine, uracil and their derivatives are of great biological importance ; however, because of their high complexity and low symmetry, only few workers have studied these compounds [1-3]. They developed interest in the molecular mechanism which play great importance in the structural property of nucleic acid bases and related compounds.

In view of the above discussion, the present paper reports the vibrational spectral studies along with the tautomeric forms and hydrogen bonding of 4,6-dihydroxy-5-nitro pyrimidine. The thermodynamic functions of this molecule have also been calculated and discussed.

2. Experimental

Spec-pure grade sample of 4,6-dihydroxy-5-nitro pyrimidine (here after referred as 4,6,5-DHNP) was obtained from Aldrich-Chemie West Germany and used as such. Its purity was confirmed by elemental analysis and melting point determination. Infrared (IR) spectrum was recorded on Perkin Elmer model M-683 spectrophotometer in the region 200-4000 cm^{-1} in KBr and polythene pellets. The laser Raman spectrum in the region 50-4000 cm^{-1}, has been recorded on a Spex Spectrophotometer using argon laser source with exciting radiations 5145 Å.

3. Results and discussion

The molecular structure of the compound 4,6,5,-DHNP is shown in Figure 1. The laser Raman spectrum of the molecule is shown in Figure 2. The proposed assignments of vibrational

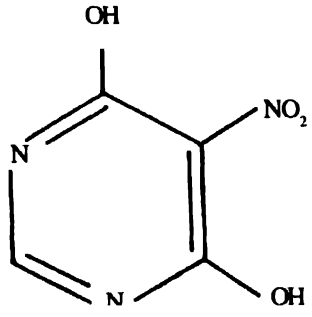

Figure 1 Molecular structure of 4,6-dihydroxy-5-nitropyrimidine.

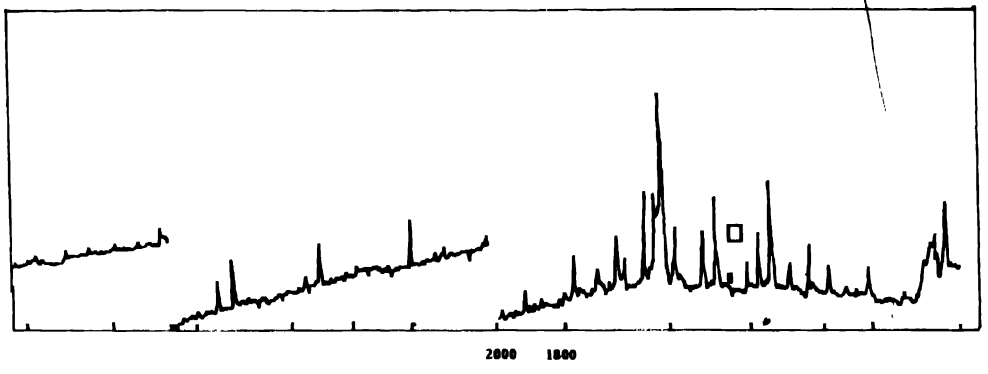

Figure 2. Laser Raman spectrum of 4, 6-dihydroxy-5-nitropyrimidine

spectra of the compounds are given in Table 1. The comparison of IR frequencies of 4,6,5,-DHNP with the similar molecules is given in Table 2. Tautomeric forms of neutral, cationic and anionic forms of the said molecule are shown in Figure 3. The statistically computed thermodynamic functions *viz.*, enthalpy function, free energy function, entropy and heat capacity with absolute temperature are given in Table 3.

3.1 Vibrational spectra :

3.1.1 Ring vibrations

The molecule under present investigation is trisubstituted pyrimidine. Therefore, only one C-H oscillation is expected. Nishimura *et al* [4] have calculated C-H stretching value for uracil at 3065 cm^{-1}. Gupta *et al* [5] have found this mode at 3090 and 3060 cm^{-1} in 4-amino-6-hydroxy-2-mercapto and 2-amino-4-hydroxy-6-methyl pyrimidine respectively. In the present study, IR band observed at 3032 cm^{-1} with the corresponding Raman value 3040 cm^{-1} has been assigned to C-H stretching mode.

The C-H in-plane and out-of plane bending modes lie in the region 1000-1500 cm^{-1} and 750-1000 cm^{-1} respectively in pyrimidine [6]. In the present study, the IR bands observed at 1140 and 800 cm^{-1} may be assigned to C-H in-plane and out-of-plane bending vibrations respectively.

The quantum mechanical calculations by Nishimura *et al* [4] show that in the N-H stretching region, the higher frequency corresponds to N_1-H stretching and lower frequency

Table 1. Assignments of vibrational frequencies of 4, 6-dihydroxy-5-nitro pyrimidine (all values in cm^{-1}).

Wilson number	IR bands	Raman bands	Assignments
–	3560 m	-	μ (O-H)
–	3180 m	--	μ (N_1-H)
–	3140 w	3100 m	μ (N_1 H)
20 a	3032 w	3040 w	μ (C H)
-	1642 m	-	μ (C=O)
8 b	1582 s	--	μ ring
8 a	1566 w	-	μ ring, β (N-H)
--	1535 w	–	μ assym NO_2
19 a	1492 w	–	μ ring
19 b	1444 w	-	μ ring
14	1350 s	1350 vs	μ sym NO_2
13	1282 m	-	μ (C-OH)
–	1270 m	–	μ (C-NO_2)
–	1248 w	-	β (O-H)
–	1192 m	–	β (O-H)
3	1140 w	-	β (C-H)
12	1025 w	–	ring t bending
–	896 m	870 w	γ (N-H)
–	858 w	845 vs	NO_2 scissoring
11	800 vs	–	γ (C-H)
–	740 w	760 w	NO_2 wagging
1	738 w	–	ring breathing
4	725 m	–	γ ring
6 b	630 vs	-	β ring
18 b	622 vw	–	β (C-OH)
–	578 w	–	NO_2 rocking
–	538 s	–	β (C=O)
–	346 w	-	γ (O-H), γ ring
–	320 w	–	γ (C-OH)
–	–	130 s	NO_2 torsion

vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

μ = stretching, β = in-plane bending, γ = out-of-plane bending, t. bending = trigonal bending.

to N_3-H mode. Goel *et al* [7] have assigned these modes at 3230 and 3102 cm^{-1} in mercapto pyrimidines. In view of this, IR band with medium intensity at 3180 cm^{-1} and another weak IR band at 3140 cm^{-1} with the counterpart of Raman band at 3100 cm^{-1}, have been taken to represent N_1-H and N_3-H stretching modes respectively, under the present investigation. The appearance of N-H stretching and bending vibrations in the present molecule is due to its tautomeric behaviour (Figure 3).

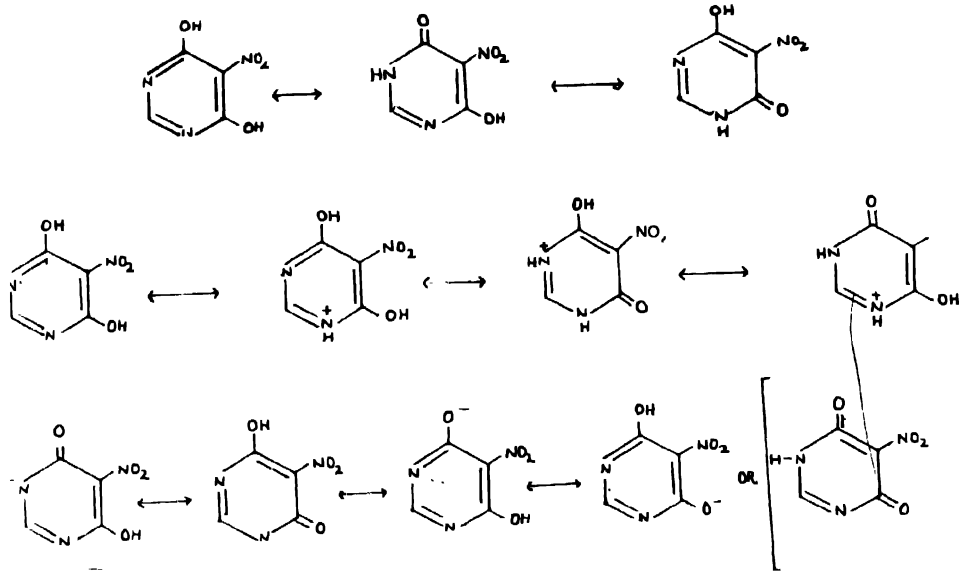

Figure 3 Tautomericforms of (a) Neutral (b) Cationic (c) Anionic forms of 4, 6, 5 DHNP

The IR band observed at 896 cm^{-1} with the corresponding Raman value 870 cm^{-1} has been taken to represent N-H out-of-plane bending mode under the present investigation. These values find support from literature value [8].

The N-heterocyclic ring breathing vibration occurs at 791, 779 and 790 cm^{-1} in cytosine, cytosine-d_3 and 2-thiocytosine respectively [9]. In the present study, a weak IR band at 738 cm^{-1} may be assigned to ring breathing mode which also find support from the literature value [10].

Table 2 Correlation of - NO_2 group frequencies (cm^{-1})

Mode of Vib.	NO_2 benzene	PC NO_2-benzene	2,4,6-DCNA	PNA	4,6,5-DCNP	4,6,5-DHNP
μ asym NO_2	1527	1524	1530	1540	1558	1535
μ sym NO_2	1351	1343	1360	1352	1352	1350
NO_2 scissoring	852	855	860	859	856	858
NO_2 wagging	704	741	730	-	-	740
NO_2 rocking	535	535	540	-	590	578

PC = para-chloro
DCNA = dichloro-nitro-aniline
PNA = para-nitro-aniline
DCNP = dichloro-nitro-pyrimidine
DHNP = dihydroxy-nitro-pyrimidine

3.1.2 C-X vibrations

Sanyal *et al* [11] have assigned C-OH stretching mode at 1305 and 1332 cm^{-1} in dihydroxy pyrimidine. In the present study, only one vibration has been clearly identified at 1282 cm^{-1} in the IR spectrum to this mode. IR bands observed at 622 cm^{-1} and 320 cm^{-1} have been assigned to C-OH in – plane and out-of-plane bending modes respectively under the present investigation [11, 12].

Table 3 Thermodynamic functions of 4,6-dihydroxy-5-nitro-pyrimidine (All values in Cal/mole -°k)

Temperature (K°)	$(H°-E°_0)/T$	$(F°-E°_0)/T$	$S°$	$C°_p$
100	8 409	45 850	54 259	10 005
200	10.773	53.034	63 808	10 20
273	12 792	56.993	69 786	20 383
298	13.486	58 231	71 717	21 731
300	13 541	58 328	71 869	21 837
400	16 250	62 883	79 134	26.805
500	18 804	67 009	85 813	31 130
600	21 176	70 831	92 007	34 840
700	23 359	74 415	97 774	37 997
800	25.361	77 799	103.161	40.667
900	27 193	81 001	108 204	42.954
1000	28 868	84 069	112 938	44 895
1100	30 403	86 988	117 391	46 553
1200	31 809	89 781	121 591	47 976
1300	33 101	92 458	125 560	49.200
1400	34 290	95 029	129 319	50 258
1500	35 386	97 501	132 88	51 175

where $E°_0$ = Zero point energy, $H°$ = Enthalpy,
$C°_p$ = Heat capacity, $S°$ = Entropy

Goel *et al* [13] have assigned C-NO_2 stretching mode at 1272 cm^{-1} in IR spectrum of 4, 6-dichloro-5-nitro pyrimidine. In 4,6,5-DHNP, this mode has been identified at 1270 cm^{-1}. Goel *et al* [14] have found C=O stretching and in-plane bending modes at 1663 and 545 cm^{-1} in dihydroxy pyrimidine. In view of this, we may assign these modes at 1642 cm^{-1} and 538 cm^{-1} in the IR spectrum of present molecule. These assignments also find support from literature value [15].

3.1.3 Group vibrations

OH group

For molecules containing OH group, the O-H valance oscillation appears in the region 3500-3700 cm^{-1} [16]. Goel *et al* [7] have assigned this mode at 3560 cm^{-1} in 4,6-dihydroxy-2-mercapto pyrimidine. In view of this, IR band observed at 3560 cm^{-1} may be assigned to O-H stretching mode under present investigation. The bands observed at 1248 cm^{-1} and 1192 cm^{-1} has been

assigned to O-H in plane bending and 346 cm $^{-1}$ to out-of-plane bending modes respectively [7].

NO_2 group

The bands observed in the range 1530-1500 cm^{-1} are called asymmetric stretching while those in the range 1370-1330 cm^{-1} are symmetric stretching mode of the nitro group [17]. The IR band at 1535 cm^{-1} has been assigned to asymmetric nitro group stretching mode while another strong IR band at 1350 cm^{-1} with the corresponding Raman value at 1350 cm^{-1} has been taken to represent NO_2 symmetric stretching mode. Goel *et al* [13] have assigned these modes at 1558 and 1352 cm^{-1} in IR spectrum of dichloro-nitro-pyrimidine.

In nitro-compounds, the bands in the range 890-835 cm^{-1}, 760-700 cm^{-1} and 280-520 cm^{-1} are usually the regions for the scissoring, wagging and rocking modes respectively [18]. These bands have been identified at 858, 740 and 578 cm^{-1} respectively under the present investigation.

The NO_2 torsion mode is expected to lie in the region 100-150 cm^{-1} [19]. In the present molecule, the Raman band at 130 cm^{-1} may be related to the NO_2 torsion mode.

4. Hydrogen bonding and tautomeric behaviour

Infrared spectra of several di- and tri- hydroxy pyrimidine show that substitution at 4 position leads to ketonic structure where as substitution at 6 position tends to retain its original enolic character. In 4, 6,5-DHNP, since there are two hydroxy groups attached at 4 and 6 positions, therefore two stretching, two in-plane bending and two out-of-plane bending modes of OH groups are expected but we could observe only one of each. Similarly, stretching, in-plane bending and out-of plane bending modes of (C-OH) and (C = O) have also been observed one of each instead of two, each due to the presence of two hydroxyl groups. The band observed at 1673 cm $^{-1}$ in case of uracil has been assigned to C = O stretching mode [20, 21]. Thus, the band at 1642 cm^{-1} in 4,6,5-DHNP corresponds to this vibration. Further more, only one NH out-of-plane bending mode is observed at 896 cm^{-1} [8]. In accordance with the above discussion, it is therefore concluded that in 4,6,5-DHNP, hydroxyl group present at position 4 is in ketonic form as its H atom has moved to N_3 of the ring, where as hydroxyl group present at 6 position has retained its original character and is present in enolic form.

5. Thermodynamic functions

Thermodynamic functions viz. enthalpy function $H^\circ - E_0^0 / T$, heat capacity C°_p, free energy function $F^\circ - E_0^0 / T$ and entropy S° of 4,6-Dihydroxy-5-nitro pyrimidine have been computed by using the standard expressions [19,21] by taking Y-axis perpendicular to the molecular plane and Z-axis to pass through the para positions. For determining rotational contribution, the following structural parameters were used [22, 23].

Bond length				**Bond angle**		
C_1N_1	=	1.32 Å		$\angle C_5N_5O_{5(i)}$	=	119°
C_2N_3	=	1.31 Å		$\angle C_5N_5O_{5(ii)}$	=	118°
C_4N_3	=	1.36 Å		$\angle O_{5(i)}N_5O_{5(ii)}$	=	123°

C_4N_5	= 1.39 Å	∠	$N_3C_4C_5$	=	119°
C_5C_6	= 1.40 Å	∠	$C_2N_3C_4$		117°
C_6N_1	= 1.30 Å	∠	$C_2N_1C_6$		115°
C_4O_4	= 1.25 Å	∠	$N_1C_6C_5$		129°
C_6O_6	= 1.25 Å	∠	$N_1C_6O_6$		119°
C_5N_5	= 1.47 Å	∠	$C_5C_6O_6$		112°
$N_5O_{5(i)}$	= 1.23 Å	∠	$N_3C_4O_4$		111°
$N_5O_{5(ii)}$	= 1.23 Å	∠	$C_5C_4O_4$		130°

All other angles were taken as 120° in the ring. The thermodynamic functions have been calculated at different temperature between 100-1500 K using fundamental frequency and assuming rigid rotor harmonic oscillator approxmation. The calculations were performed for one mole of an ideal gas at one atmospheric pressure. The symmetry number for over all rotation has been taken as 2 and for internal rotation as 1. The principal moment of inertia were found to be 66.51, 109.05 and 42.48×10^{-39} gm. cm^2 in this molecule while the reduced moment of inertia is 0.5597×10^{-37} gm.cm^2. The thermodynamic functions of 4,6,5-DHNP given in Table 3 are in the same trend as reported in the literature [23-25].

References

[1] R K Goel and C Gupta *J Raman Spectrosc* **16** 1 (1985)

[2] Salik Ahmad and M Isaq *Spectrochim Acta*, Part A, **52** 1369 (1996)

[3] S Mohan and V Ilangovan, *Indian J Pure Appl Phys* **32** 91 (1994)

[4] Y Nishimura, M Tuboi, S Kato and K Morokuma *J Am Chem Soc*, **103** 1354 (1981)

[5] S P Gupta, Sangeeta Sharma and R K Goel *Indian J Chem* **26A** 220 (1987)

[6] L J Bellamy *Infrared Spectra of Complex Molecules* (London Chapman & Hall) (1975)

[7] R K Goel, C Gupta and S P Gupta *Indian J Pure Appl Phys*, **23** 344 (1985)

[8] J Bandikar and G Zundal *Spectrochim Acta*, **39A** 337 (1983)

[9] R C Lord and G J Thomas (Jr.) *Spectrochim Acta* **38A** 815 (1982)

[10] A J Barnes, M A Stuckey and L Legall *Spectrochim Acta* **40** 419 (1984), N Syam Sunder *Indian J Pure Appl Phys* **22** 193 (1984)

[11] N K Sanyal, S L Srivastava and D N Verma *Indian J Phys* **50** 865 (1976)

[12] R K Goel, S K Gupta, M L Agarwal and S N Sharma *Indian J Pure Appl Phys* **19** 501 (1981)

[13] R K Goel, S D Sharma, V K Jain, B S Yadav and Subhash Chand *Acta Ciencia India* **15** 183 (1989)

[14] R K Goel, K P Kansal and S N Sharma, *Indian J. Pure Appl Phys* **18** 1032 (1980)

[15] Vir Singh, Seema, B S Yadav and Subhash Chand in *Annual Session of National Academy of Sciences* (Paper Presented) (1996)

[16] Seema, U K Jetley, B S Yadav and S P Gupta *Oriental J Chem* **7(2)** 71 (1991)

[17] J F Brown *J Am Chem. Soc*, **77** 341 (1955)

[18] J H S Green and D J Harrison *Spectrochim Acta* Part A, 925 (1970)

[19] G Herzberg *Molecular Spectra and Molecular Structure – Infrared and Raman Spectra* (Princeton, NJ · D Van Nostrand) p 911 (1966)

[20] C N R Rao *Chemical Applications of Infrared Spectroscopy*, (New York : Academic) (1963)

[21] K S Pitzer and W D Cwinn *J Chem. Phys* **10** 428 (1942)

[22] N L Owen and R E Hester, *Spectrochim Acta*, **25A** 343 (1969)

[23] C L Chatterjee, P P Garg and R M P Jaiswal *Spectrochim Acta*, **34A** 943 (1978)

[24] S Mohan and N Sundaraganesan *Indian J Pure Appl Phys* **29** 807 (1991)

[25] B S Yadav, Vir Singh, Seema and Subhash Chand *Indian J. Phys* **71B** 69 (1997)